

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification : C07C 7/20, C10G 75/04</p>	<p>A1</p>	<p>(11) International Publication Number: WO 98/14416</p> <p>(43) International Publication Date: 9 April 1998 (09.04.98)</p>
<p>(21) International Application Number: PCT/US97/16292</p> <p>(22) International Filing Date: 16 September 1997 (16.09.97)</p> <p>(30) Priority Data: 08/720,885 4 October 1996 (04.10.96) US</p> <p>(71) Applicant: BETZDEARBORN INC. [US/US]; 4636 Somerton Road, P.O. Box 3002, Trevose, PA 19053-6783 (US).</p> <p>(72) Inventor: ARHANCET, Graciela, B.; 20667 Castle Bend Drive, Katy, TX 77450 (US).</p> <p>(74) Agents: VON NEIDA, Philip, H. et al.; BetzDearborn Inc., 4636 Somerton Road, P.O. Box 3002, Trevose, PA 19053-6783 (US).</p>		<p>(81) Designated States: BR, CA, ID, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: COMPOSITIONS AND METHODS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION</p> <p>(57) Abstract</p> <p>The polymerization of vinyl aromatic monomers such as styrene is inhibited by the addition of a composition of a stable hindered nitroxyl radical and an oxime compound.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COMPOSITIONS AND METHODS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

FIELD OF THE INVENTION

The present invention relates to compositions and methods for inhibiting the polymerization of vinyl aromatic monomer compounds.

BACKGROUND OF THE INVENTION

5

Common industrial methods for producing styrene typically include separation and purification processes such as distillation to remove unwanted impurities. Unfortunately, purification processes carried out at elevated temperatures result in an increased rate of undesired polymeri-
10 zation. Distillation is generally carried out under vacuum to minimize loss of monomer. The presence of oxygen, which is typically excluded from styrene distillation, will also promote polymerization of the monomer.

This polymerization results not only in loss of desired monomer end-product, but also in the uses of production efficiency caused by polymer formation and/or agglomeration of polymer on process equipment. Thermal polymerization, which typically occurs during distillation, of styrene monomer results in the formation of normal (i.e., linear) polymer. This resulting polystyrene polymer is characterized by its glassy and transparent appearance and its solubility in the styrene monomer and many organic solvents.

10 The compounds generally used commercially to inhibit polymerization of vinyl aromatic monomers are of the dinitrophenol family. For example, U.S. Pat. No. 4,105,506, Watson et al. teaches the use of 2,6-dinitro-p-cresol as a polymerization inhibitor for vinyl aromatic compounds. U.S. Pat. No. 4,466,905, Butler et al. teaches that a combination of 2,6-
15 dinitro-p-cresol and p-phenylenediamine will inhibit polymerization in a distillation column when oxygen is present. U.S. Pat. No. 4,774,374, Abruscato et al. teaches compositions for inhibiting the polymerization of vinyl aromatic compounds. The composition is an oxygenated product of the reaction of N-aryl-N'-alkyl-p-phenylenediamine with oxygen. U.S. Pat.
20 Nos. 5,426,257 and 5,489,718, Arhancet, teach methods and compositions for inhibiting the polymerization of vinyl aromatic monomers comprising an oxime compound and a hydroxylamine compound and/or a phenylenediamine.

25 U.S. Pat. No. 5,254,760, Winter et al. teaches compositions and processes for inhibiting vinyl aromatic compound polymerization. The processes comprise adding to the vinyl aromatic compounds during purification or distillation a mixture of a stable hindered nitroxyl compound

and an aromatic nitro compound. U.S. Pat. No. 4,670,131, Ferrell, teaches methods for inhibiting fouling of hydrocarbons containing unsaturated compounds with a stable free radical. The stable free radical can be a nitroxide compound.

5

A variety of inhibitor compositions have been employed in styrene and other vinyl aromatic monomers to inhibit undesired polymerization. Agents that have been used include sulfur, p-benzoquinone, tert-butyl pyrocatechol, phenothiazine, and hindered phenols. However, many of these compounds present disadvantages such as high intoxicity, instability, explosive hazard at elevated temperature and insufficient efficacy under processing conditions (i.e., inhibitor requires oxygen to be effective). The present inventor has discovered a novel composition which acts to inhibit vinyl aromatic monomer polymerization while avoiding the problems of certain known inhibitors.

15

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to compositions and methods for inhibiting the polymerization of vinyl aromatic monomer compounds comprising adding to the monomers a combination of a stable hindered nitroxyl radical and an oxime compound.

20

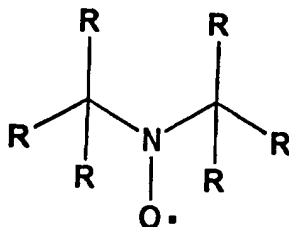
The compositions of the present invention are effective at inhibiting polymerization of vinyl aromatic monomers under processing conditions. These processing conditions include but are not limited to preparation, purification, distillation and vacuum distillation processes. The compositions of the present invention are effective in both processes where

25

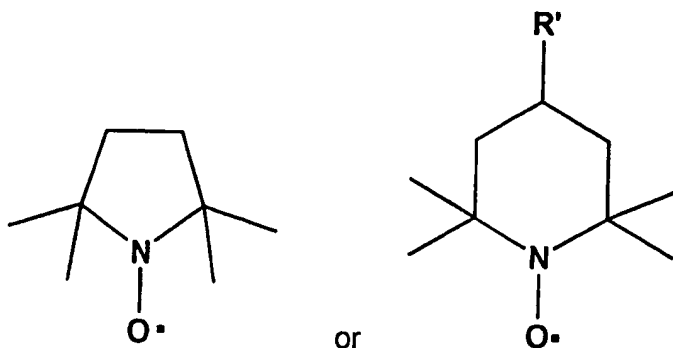
oxygen is present and under oxygen-free conditions. The term "oxygen-free" is meant to define the substantially oxygen free conditions under which vinyl aromatic monomers, particularly styrene, are often processed. These conditions, exemplified by distillation and purification processes generally have less than 2 parts per million parts of oxygen present and preferably less than 1 part of oxygen per million parts styrene.

The vinyl aromatic monomers that are treated by the compositions of the present invention include but are not limited to styrene, bromostyrene, divinylbenzene, and α -methylstyrene. The compositions of the present invention are particularly efficacious at inhibiting the polymerization of styrene monomer.

The stable hindered nitroxyl radical generally has the formula:



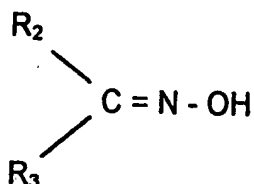
where R is a C₁ to C₃ alkyl group; or a cyclic compound having the formula:



where R' is H, hydroxyl, =O, OCOR'', R'' is a C2 to C17 alkyl group; benzoate, phthalate, terephthalate, sebacate, succinate, and adipate.

The oxime compounds generally have the formula:

5



10

wherein R₂ and R₃ are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylhydroxyaryl or arylhydroxyalkyl groups having three to about twenty carbon atoms. Examples of these compounds include but are not limited salicylaldoxime and 5-nonylsalicylaldoxime.

15

The total amount of stable hindered nitroxyl radical and oxime compound used in the methods of the present invention is that amount which is sufficient to inhibit polymerization and will vary according to the conditions under which the vinyl aromatic monomer is being processed, and the temperature of the system. At higher processing temperatures and higher monomer contamination, larger amounts of the polymerization inhibiting composition are generally required.

20

Styrene, for example, is typically processed at temperatures between 95° and 125°C. The compositions of the present invention are effective at inhibiting the polymerization of styrene over this range of temperatures.

25

For purposes of the present invention, the term "effective inhibiting amount" is defined as that amount which is effective at inhibiting polymerization. Preferably the effective amount ranges from about 1 part to about 10,000 parts per million parts of monomer. More preferably, the effective amount ranges from about 1 part to about 1000 parts per million parts of monomer.

The weight ratio of the stable hindered nitroxyl radical to oxime compound will generally range from about 9:1 to about 1:9 with a weight ratio of about 1:1 preferred.

The compositions of the present invention can be added to the vinyl aromatic monomer by any conventional method at any point of the processing system, either as separate and individual ingredients or as a combination of ingredients.

The compositions of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer to be treated may be employed.

Accordingly, it is possible to produce a more effective vinyl aromatic monomer polymerization inhibiting treatment than is obtained by the use of either compound by itself when measured at comparable treatment levels. This synergism or enhanced activity between components

allows for the concentration of each of the components to be lowered and the total quantity of polymerization inhibitor required, particularly at higher temperatures, may be lowered while achieving a commensurate level of polymerization inhibition.

5

Examples

The invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative, and not as restricting the scope of the invention.

10

5 mL of uninhibited styrene was placed in a test tube and the appropriate amount of treatment was added. The tube was capped with a rubber septum and argon was bubbled through the liquid at 10 mL/min for 3 minutes. The tubes utilized in Example 1 were then placed in an oil bath heated to 110°C for 2 hours. The amount of polystyrene formed was determined by methanol precipitation. The results of this testing are presented in Table I.

20

TABLE I

Styrene Polymerization Test
Uninhibited Styrene at 110°C

	<u>Inhibitor</u>	<u>Dosage (ppm)</u>	<u>% Polymer Formed</u>
	Blank	—	8.87
25	SA	200	8.43
	TEMPO	200	0.76
	TEMPO/SA	200/200	0.05
	TEMPO/SA	134/66	0.77
	TEMPO/SA	100/100	1.15
30	TEMPO/SA	66/134	2.04
	TEMPO	100	1.77
	tAtBN	200	0.29

TABLE I (cont'd)

Styrene Polymerization Test
Uninhibited Styrene at 110°C

	<u>Inhibitor</u>	<u>Dosage (ppm)</u>	<u>% Polymer Formed</u>
5	tAtBN/SA	134/66	0.37
	tAtBN/SA	100/100	0.48
	tAtBN/SA	66/134	0.62
	OHTEMPO	200	0.86
	OHTEMPO/SA	200/200	0.25
10	OHTEMPO/SA	100/100	1.91
	OHTEMPO/NSA	200/200	0.12

TEMPO is 2,2,6,6-tetramethyl-1-piperidinoxy, free radical

tAtBN is tert-amyl-tert-butyl aminoxyl, free radical

15 OHTEMPO is 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoxy, free radical

SA is salicylaldoxime

NSA is 5-nonylsalicylaldoxime

The procedure of Example 1 was repeated using an oil bath
20 heated at 120°C. The results of Example 2 are reported in Table II.

TABLE II

Styrene Polymerization Test
Uninhibited Styrene at 120°C

	<u>Inhibitor</u>	<u>Dosage (ppm)</u>	<u>% Polymer Formed</u>
25	Blank	—	17.78
	TEMPO	600	1.23
	TEMPO/SA	400/200	0.68
	TEMPO/SA	300/300	0.35
	TEMPO/SA	200/400	2.70
30	TEMPO	300	3.49
	tAtBN	600	0.44
	tAtBN/SA	400/200	0.75
	tAtBN/SA	300/300	0.53
	tAtBN/SA	200/400	1.03
35	tAtBN	600	0.95

For Example 3, uninhibited styrene (100 mL) was placed in a 250 mL three-necked flask fitted with a bubbler, a septa, and a condenser. 200 ppm of TEMPO and 200 ppm of SA were added and argon was bubbled through the solution at 10 mL/min for 10 minutes. While argon sparging continued, the flask was immersed in an oil bath heated at 110°C. 5.0 mL samples were taken every 30 minutes and the amount of polymer formed was determined by methanol precipitation. After heating for three hours, polymer content was 0.04%.

For Example 4, the procedure of Example 3 was followed except 300 ppm of TEMPO and 300 ppm of SA were immersed in an oil bath heated at 120°C. After heating for 2 hours, polymer content was 0.15%.

Another study was performed demonstrating that the inventive composition provided better results than the individual stable hindered nitroxyl radical. For Example 5, the procedure of Example 3 was followed except samples were taken every hour. The results of this testing are presented in Table III.

20

TABLE III

Reflux Under Argon Test
Uninhibited Styrene at 110°C

	Time (Hours)	Percent Polymer Formed	
		OHTEMPO (400 ppm)	OHTEMPO/SA (200/200 ppm)
25	0	0	0
	1	0	0
	2	0	0
	3	0.24	0.04
30	4	0.56	1.05

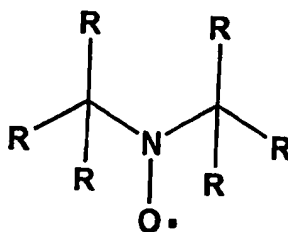
These results demonstrate that superior polymerization inhibition was achieved for up to 3 hours for the inventive composition.

5 While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

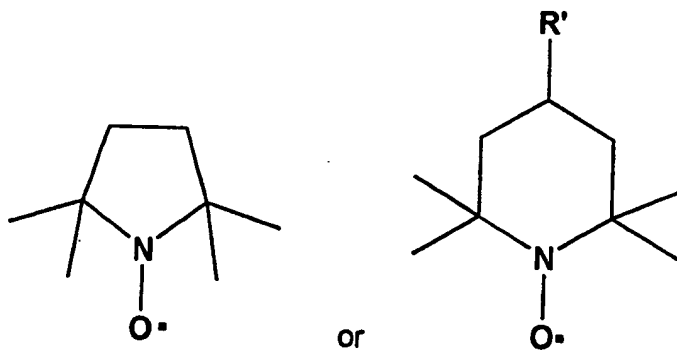
Having thus described the invention, what I claim is:

1. A composition comprising a stable hindered nitroxyl radical and an oxime compound.

2. The composition as claimed in claim 1 wherein said stable hindered nitroxyl radical has the formula:



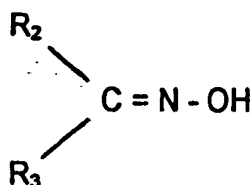
5 where R is a C₁ to C₃ alkyl group; or a cyclic compound having the formula:



where R' is H, hydroxyl, =O, OCOR'', R'' is a C₂ to C₁₇ alkyl group;
10 benzoate, phthalate, terephthalate, sebacate, succinate, and adipate.

3. The composition as claimed in claim 1 wherein said oxime compound has the formula:

5



wherein R_2 and R_3 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylhydroxyaryl or arylhydroxyalkyl groups and have three to about twenty carbon atoms.

4. The composition as claimed in claim 3 wherein said oxime compound is selected from the group consisting of salicylaldoxime and 5-nonylsalicylaldoxime.

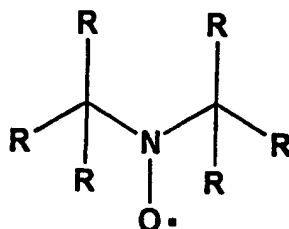
5. The composition as claimed in claim 1 further comprising a vinyl aromatic monomer.

6. The composition as claimed in claim 1 wherein the weight ratio of stable hindered nitroxyl radical to oxime compound ranges from about 9:1 to about 1:9.

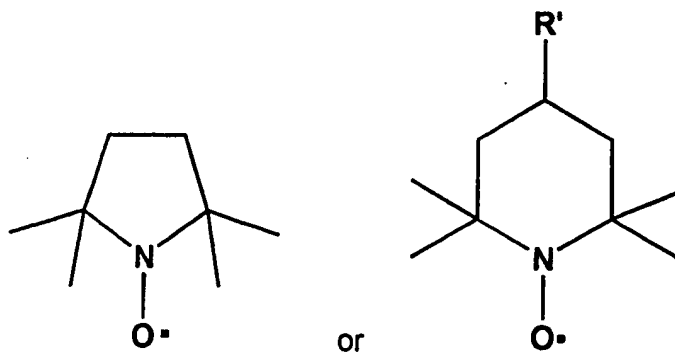
7. The composition as claimed in claim 1 wherein the weight ratio of stable hindered nitroxyl radical to oxime compound ranges from about 1:1.

8. A method for inhibiting the polymerization of vinyl aromatic monomer comprising adding to said monomers an effective inhibiting amount of a composition comprising a stable hindered nitroxyl radical and an oxime compound.

9. The method as claimed in claim 8 wherein said stable hindered nitroxyl radical has the formula:

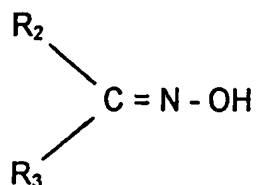


5 where R is a C₁ to C₃ alkyl group; or a cyclic compound having the formula:



where R' is H, hydroxyl, =O, OCOR'', R'' is a C₂ to C₁₇ alkyl group;
 10 benzoate, phthalate, terephthalate, sebacate, succinate, and adipate.

10. The method as claimed in claim 8 wherein said oxime compound has the formula:



5

wherein R₂ and R₃ are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylhydroxyaryl or arylhydroxyalkyl groups and have three to about twenty carbon atoms.

11. The method as claimed in claim 10 wherein said oxime compound is selected from the group consisting of salicylaldoxime and 5-nonylsalicylaldoxime.

12. The method as claimed in claim 8 wherein said vinyl aromatic monomer is styrene.

13. The method as claimed in claim 8 wherein said monomer is undergoing processing.

14. The method as claimed in claim 13 wherein said processing is at a temperature ranging from about 95°C to about 125°C.

15. The method as claimed in claim 8 wherein oxygen is present in said vinyl aromatic monomer.

16. The method as claimed in claim 8 wherein said composition is added to said monomer in an amount ranging from about 1 part to about 10,000 parts per million parts of monomer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/16292

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO7C 7/20; C10G 75/04

US CL : 585/435, 3, 4, 5, 832; 208/48AA

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/435, 3, 4, 5, 832; 208/48AA

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: polymeriz?(5a)(inhibit? or retard? or prevent?)(p)(notroxy!?)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,545,786 A (WINTER ET AL) 13 August 1996, abstract, claims.	1-16
Y	US 5,489,718 A (ARHANCET) 06 February, 1996, col. 2, lines 22-24, 43-47; col. 3, lines 25-50.	1-16
A	US 4,237,326 A (FUGA ET AL) 02 DECEMBER 1980	1-16
A, P	US 5,583,247 (NESVADBA ET AL) 10 December 1996.	1-16

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 OCTOBER 1997

Date of mailing of the international search report

26 JAN 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

BEKIR L. YILDIRIM

Telephone No. (703) 308-0661